

# Collective Spin and Charge Excitations in Planar Aromatic Molecules

K. Haghighi Mood,<sup>1</sup> S. A. Jafari\*,<sup>2,3</sup> E. Adibi,<sup>4</sup> G. Baskaran,<sup>5</sup> and M. R. Abolhassani<sup>1</sup>

<sup>1</sup>Department of Physics, Science and Research Branch (IAU), Tehran, Iran

<sup>2</sup>Department of Physics, Sharif University of Technology, Tehran 11155-9161, Iran

<sup>3</sup>School of Physics, Institute for Research in Fundamental Sciences, Tehran 19395-5531, Iran

<sup>4</sup>Department of Physics, Isfahan University of Technology, Isfahan 84156, Iran

<sup>5</sup>Institute of Mathematical Sciences, Chennai 600113, India

Employing high accuracy fixed node diffusion Monte Carlo (DMC) method we calculated the lowest triplet collective excitation (spin gap), as well as an upper bound for the singlet excitations (charge gap) in a series of charge neutral planar non-ladder aromatic compounds. Both excitation energies lie below the continuum of particle-hole excitation energies obtained from Hartree-Fock orbitals. Hence they can be interpreted as genuine bound states in the particle-hole channel. Assuming a resonating valence bond (RVB) ground state which has been recently suggested for  $sp^2$  bonded systems [M. Marchi, *et. al.*, Phys. Rev. Lett. **107**, 086807 (2011)], offers a unified description of both excited states as two-spinon and doublon-holon bound states. We corroborate our interpretation, by Exact diagonalization study of a minimal model on finite honeycomb clusters.

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**Introduction:** Correlation effects are characteristic of  $\pi$  conjugated systems composed essentially of hexagonal arrangements of  $sp^2$  bonds [1]. Pauling took the initiative to describe the bonding in benzene ( $C_6H_6$ ), a prototype of these systems, in terms of valence bonds (VB), focusing his attention on the spin part of the bonding wave function, namely a singlet. Such singlet valence bonds can be formally described as the ground state of an effective Heisenberg exchange interaction  $JS_1.S_2$ , where  $J$  is the exchange integral between the overlapping atomic orbitals [2]. When the coordination number is low, in the above effective (model) Hamiltonian, the condition is more conducive for superposition of valence bond singlets to constitute the ground state – a unique opportunity provided by three-fold coordination in these aromatic systems. Hence Pauling’s formulation of the energy levels of molecules in terms of quantum mechanical superposition of valence bond configurations, the so called resonating valence bond (RVB) [3] becomes an important alternative route to understand energy levels of molecules.

Some recent works [4–6] have combined the power of Monte Carlo methods with the basic notion of RVB [7], to construct variational wave functions in terms of geminals (determinants composed of “pairing” wave functions). Optimization of such RVB based many-body wave-functions, determine the properties of  $sp^2$  bonded systems with remarkable accuracy [4–6]. More specifically this technique captures the Kekule and Dewar contributions to the ground state of benzene [6]. Therefore, the notion of RVB in these systems is capable of capturing interesting many-body effects in the ground state, at much lower computational cost, compared to more involved quantum chemical methods. The application of the above method to undoped graphene indicates that the ground state is a short range, gapped spin liquid [6] which agrees with

other proposals based on the Hubbard model [8–10].

In view of the above mentioned evidences for a possible spin liquid *ground state* in planar  $sp^2$  bonded systems, the next natural question would be about the nature of excited states. As a simple prototype which demonstrates the inadequacy of single-particle description of energy states in this family of molecules, consider benzene,  $C_6H_6$  for which the MO would predict a singlet ground state for six  $p_z$  electrons on the hexagonal ring. Within MO picture, the first singlet excited state ( $S_1$ ) and the first triplet excited state ( $T_1$ ) are expected to be degenerate. However, observation of a remarkable splitting between the low-lying triplet and singlet excited states [12] indicates the importance of correlation effects even in the excited states of these molecules. Since such correlation effects are based on local interactions, one expects the same picture to hold even in extremely extended members of this family, such as graphene [13] and carbon nano-tubes. The weak coupling (itinerant) limit of the graphene is well known to represent a Dirac liquid [16], and can be described by standard single-particle approach [13]. However, *ab-initio* calculations [14] show that the strength of short-range part of the Coulomb interaction in these materials is  $\sim 10$  eV, which is remarkably high and comparable to the estimated values of these parameters in conjugated polymers [15]. For such large values of Hubbard parameter  $U$  in these systems, emergence of a non Fermi liquid state, such as spin liquid [8, 9, 11] becomes conceivable.

In this paper, we investigate the nature of low-lying excited states in small molecules belonging to the family of  $sp^2$ -bonded carbon systems. Here we employ the state of the art QMC method to investigate the nature of many-body excitations in such hydrocarbons. This numerically accurate method suggests that the lowest excitation in such molecules is a triplet state, separated by a substantial gap from the next singlet excited state, for which we obtain an upper bound. We argue that these two lowest excited states, namely,  $T_1$  and  $S_1$  can be naturally understood in terms of a picture based on

\*Electronic address: jafari@sharif.edu

spin-charge separation. This suggests that the ground state could be viewed as a resonating valence bond state, in agreement with a recent proposal by Marchi and coworkers [6].

*Method:* Considering computational cost and accuracy, Variational Monte Carlo (VMC) and Diffusion Monte Carlo (DMC) [20] algorithms are methods of choice for the calculation of many body properties of medium electronic systems. These QMC methods can achieve chemical accuracy with a typical computational cost ranging from the second to fourth power of the number of particles [24]. In this paper we use these methods as implemented in CASINO package to calculate spin and charge gap of some aromatic compounds. The CASINO code employs important sampling DMC method [21, 22] to project out the many-body lowest energy state. In this method, the important sampled imaginary time Schrodinger equation is of the following form:

$$f(\mathbf{R}, t + \Delta\tau) = \int K(\mathbf{R}, t + \Delta\tau; \mathbf{R}', t) f(\mathbf{R}', t) d\mathbf{R}', \quad (1)$$

where  $f(\mathbf{R}, t + \Delta\tau) = \Psi_t(\mathbf{R})\psi(\mathbf{R}, t + \Delta\tau)$ ,  $\Psi_t(\mathbf{R})$  is the trial wave function and  $\psi(\mathbf{R}, t + \Delta\tau)$  is system wave function. The kernel  $K(\mathbf{R}, t + \Delta\tau; \mathbf{R}', t)$  is the propagator. As  $\Delta\tau$  approaches to infinity,  $\psi(\mathbf{R}, t + \Delta\tau)$  tends to ground state in any sector corresponding to a definite set of quantum numbers. For an efficient DMC calculation we need an optimized trial wave function. We used the multiplication of spin up and down Slater determinants and a Jastrow factor as a trial wave function:

$$\Psi_t = e^{j(\mathbf{R})} \mathbf{D}^\uparrow(\mathbf{r}_1, \dots, \mathbf{r}_N) \mathbf{D}^\downarrow(\mathbf{r}_1, \dots, \mathbf{r}_N). \quad (2)$$

Here  $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  denotes the spatial coordinates of all the electrons. The single-particle orbitals employed in the above Slater determinants have been constructed from Hartree-Fock (HF) mean field solutions which serve as a reference basis for "free" particle-hole excitations. Note that this is not the exact Jastrow-Slater trial wave function form, as it is antisymmetric only with respect to the exchange of electrons with the same spin. Such wave functions can be used to obtain expectation values with lower computational cost for any spin independent operators [20]. CASINO uses Jastrow factors of the form proposed in Refs. [22, 23]. We have taken into account the electron-electron terms  $u$ , electron-nucleus terms  $\chi$  centered on the nuclei and 3 body electron-electron-nucleus terms  $f$  in our calculations:

$$j(r_i, r_j) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N u(r_{i,j}) + \sum_{I=1}^{N_{\text{ions}}} \sum_{j=i+1}^N \chi_I(r_{i,I}) + \sum_{I=1}^{N_{\text{ions}}} \sum_{i=1}^{N-1} \sum_{j=i+1}^N f_I(r_{i,I}, r_{j,I}, r_{i,j}). \quad (3)$$

Optimization with respect to the parameters contained in the Jastrow factor was achieved by a VMC variance minimization procedure [20]. After VMC optimization we used the so optimized wave function as a DMC trial wave function. Optimization of Jastrow factors without optimizing orbitals did

not affect the accuracy in our calculations. However, optimization of Jastrow factors provides a better trial wave function for DMC calculation by making it more efficient. At the final stage of calculation, DMC projects out the ground state from this trial wave function.

Using the above method, we calculate the many-body ground state in a given sector corresponding to the conserved total  $S_z$  and total number of particles  $N$ . To extract information about spin-charge splitting from total energies, we proceed as follows: Let  $E_0(N_\uparrow, N_\downarrow)$  denote the ground state energy for a system where  $N_\sigma$  is the number of electrons, each carrying spin  $\hbar\sigma/2$  with  $\sigma = \pm$  corresponding to  $\uparrow$  and  $\downarrow$  spin orientations, respectively.  $N = \sum_\sigma N_\sigma = N_\uparrow + N_\downarrow$ , as well as the total spin component,  $S_z = (N_\uparrow - N_\downarrow)/2$  are constants of motion and hence do not change the numerical projection by DMC procedure. Therefore quantum numbers  $(N_\uparrow, N_\downarrow)$  appropriately label various sectors of the spectrum.

Let us define the the spin gap ( $\Delta_s$ ) and charge gap ( $\Delta_c$ ) as,

$$\Delta_s \equiv E_0(N_\uparrow + 1, N_\downarrow - 1) - E_0(N_\uparrow, N_\downarrow), \quad (4)$$

$$\Delta_c \equiv [E_0(N_\uparrow + 1, N_\downarrow) + E_0(N_\uparrow - 1, N_\downarrow)] - 2E_0(N_\uparrow, N_\downarrow) \quad (5)$$

where  $(N_\uparrow, N_\downarrow)$  correspond to neutral system. In all compounds considered here, the total number of electrons,  $N$ , is even, so that the unpolarized configuration (i.e. the state with equal number of spin up and spin down electrons,  $N_\uparrow = N_\downarrow$ ) turns out to be the ground state. The energy  $E_0(N_\uparrow, N_\downarrow)$  of this state can be calculated as follows: We generate a trial wave function from HF method with fixed total charge (neutral) and one spin multiplicity. Now to calculate the spin gap, Eq. (4) we flip one of the spins from, e.g.  $\downarrow$  sector, without altering the total charge. The lowest energy obtained by QMC procedure in this sector will correspond to  $E_0(N_\uparrow + 1, N_\downarrow - 1)$ . Note that in this sector, the total charge is zero and spin multiplicity is three. Note that since the spin and spatial symmetries of the many-body Hamiltonian are not broken by HF solutions, the corresponding symmetry attributes are not changed by QMC projection. This means that the energy of the  $(N_\uparrow + 1, N_\downarrow - 1)$  state will represent any of the three degenerate states belonging to the triplet representation of the  $SU(2)$  group. Spin gap defined above, represents the exact value of triplet excitation energy.

Now let us discuss the physical meaning of the charge gap defined above: Imagine an infinitely large system, with equal number of  $\uparrow$  and  $\downarrow$  spin electrons. When an electron is moved from one point in the system to a distant location, the resulting excitation will be a doublon-holon pair.  $\Delta_c$  is half of the average energy of a pair, and hence can be interpreted as an upper bound for the energy of a single holon. To calculate the energy of such doublon-holon pair, an approximate scheme is to isolate two small sub-systems surrounding the holon, and the doublon. In the absence of interactions, the doublon-holon energy will be given by the first term in the right hand side of Eq. (5). However, in reality there will be an attractive interaction between them which lowers their true energy. There-

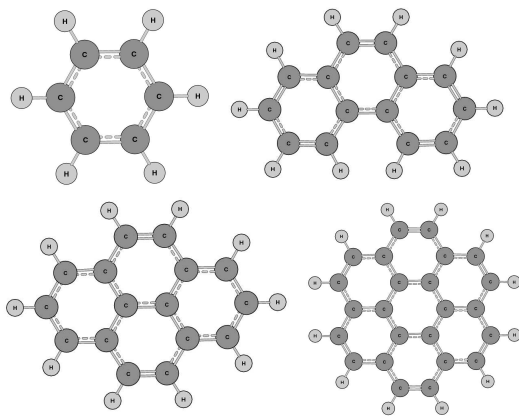


FIG. 1: Benzene  $C_6H_6$ , Phenanthrene  $C_{14}H_{10}$ , Pyrene  $C_{16}H_{10}$ , Coronene  $C_{24}H_{12}$

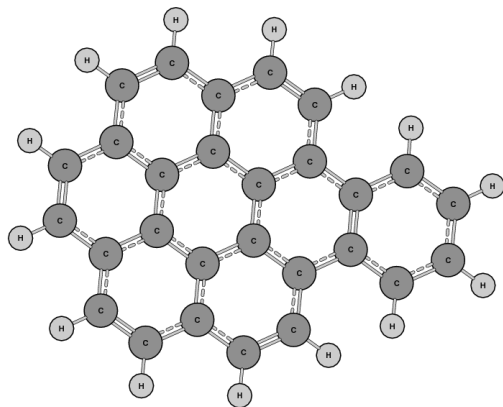


FIG. 2: Coronene with additional benzene ring  $C_{28}H_{14}$  (benzo-coronene)

TABLE I: Spin and charge excitations (eV)

Compound	Spin Gap	$\Delta_c$
$C_6H_6$	3.8(8)	5.4(6)
$C_{14}H_{10}$	3.4(1)	4.3(5)
$C_{16}H_{10}$	2.4(9)	3.8(2)
$C_{24}H_{12}$	3.0(6)	3.6(7)
$C_{28}H_{14}$	2.7(8)	3.4(0)

fore  $2\Delta_c$  defined above, is an upper bound for the energy of doublon-holon pair with respect to the neutral background. Because of the time-reversal symmetry of the Hamiltonian employed here, for such excitations based on charge fluctuations the spin orientation of the added/removed electron does not matter.

*Results:* For five planar aromatic compounds depicted in Figs. 1,2 we have calculated the above charge and spin gaps within the all electron fixed node DMC scheme. The results are reported in Table I. The spin gaps obtained here are in good agreement with experimentally reported values [12]. Also the charge gap  $\Delta_c$  obtain here as an upper bound for the  $S_1$  state agrees with existing results. For example in case of benzene,  $\Delta_c = 5.4$  eV represents a fair upper bound for the calculated result  $E_{S_1} = 4.9$  eV [12]. Therefore the method prescribed here to calculate the spin gap does indeed give the "lowest" excited state, and also the doublon-holon interpretation employed here does represent a true upper bound for the energy of  $S_1$  state. For geometry optimization as well as trial wave function generation, we used 6-311G\*\* Gaussian basis which has been done by Gaussian 03 code [19]. Note that we performed separate optimizations for ground, and excited states. All required energies are obtained with an accuracy better than  $\sim 5$  meV per atom. For each of the compounds reported in Table I, and corresponding to each set of quantum numbers ( $N_\uparrow, N_\downarrow$ ), we have optimized the geometry and the trial wave function constructed based on HF method. Then the Jastrow parameters have been optimized using variance

minimization VMC. All reported DMC results are all-electron calculations, and we did not use any pseudo-potential. DMC time step is taken to be  $0.002 \text{ Hartree}^{-1}$ . Optimized geometries have been verified to ensure they do not contain imaginary frequencies.

To interpret the data in Table I let us represent them in a different way. In Fig. 3 we plot charge and spin gaps versus the number of carbons. The new physical interpretation come about, when we also plot the tower of particle-hole excitations obtained from the (weakly correlated) Hartree-Fock theory for single particle states. This tower is the molecular analogue of the continuum of free particle-hole pairs. As can be seen by increasing the system size, the tower of particle-hole excitations approaches to a continuum. Moreover, the charge and spin gaps we obtain always remain below the the continuum of "free" particle-hole pairs. Therefore, they can be interpreted as the "bound state" of underlying free particle-hole pairs which are caused by many-body effects. First important point which is suggested by this figure is that, a very large energy difference between lower edge of the tower, and the many-body states found here implies they are long-lived excitations which do not decay into the tower. Therefore, they can be associated with new quasi-particles. Note that the blue circles ( $\Delta_c$ ) is an upper bound for the true energy of a duoblon (holon), so that the true energy of the doublon state is even lower than  $\Delta_c$ . The question is, what are these quasi-particles?

Consider the lowest excited state  $T_1$ , which is a triplet many-body state for all system sizes considered here. The  $T_1$  state can be understood in terms of a simple RPA-like bound state formation in the triplet channel of particle-hole pairs. A short range repulsion of Hubbard type translates into the attraction in the triplet particle-hole channel, and binds them together [10]. However the  $S_1$  state whose exact location in Fig. 3 is somewhere between the blue circle and red square can not be understood in terms of simple RPA-like treatments, as the RPA in singlet channel predicts an anti-bound-state *above*

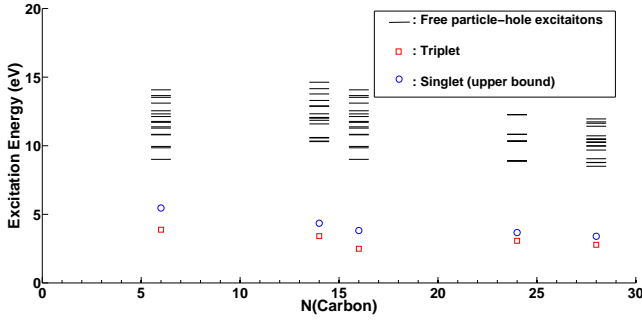


FIG. 3: Charge and spin gaps versus the number of carbon atoms in aromatic compounds studied here. To generate the “free” particle-hole continuum, we have used the Hartree-Fock orbitals. For all studied compounds, energy of spin excitation,  $T_1$  is below the singlet (charge) excitation  $S_1$ , and they both are below the continuum of free particle-hole excitations.

the tower of free particle-hole states [10]. Therefore the second excited state  $S_1$  is a genuine many-body effect, much beyond the simple RPA like treatments. The method used here to obtain the upper bound for the singlet charge excitations suggests that the  $S_1$  can be associated to an average energy of a doublon and a holon. To corroborate this claim further, let us use a simplified model Hamiltonian, which can capture the essence of the present QMC calculation in a more transparent way. First of all note that the minimal model which captures  $T_1$  state is a Hubbard model. Moreover, our earlier study of the particle-hole excitation spectrum in 1D chains suggests that the singlet collective states below the particle-hole continuum are controlled by the nearest neighbor Coulomb interaction [18]. Therefore the minimal effective model which captures both states is an extended Hubbard model,

$$H = -t \sum_{\langle i,j \rangle \sigma} c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.} + U \sum_j n_{j\uparrow} n_{j\downarrow} + V \sum_{\langle i,j \rangle} n_i n_j. \quad (6)$$

Here  $i, j$  denote sites of a 2D honeycomb lattice and  $\langle i, j \rangle$  indicates that they are nearest neighbors.  $c_{j\sigma}^\dagger$  creates an electron in the Wannier state corresponding to the  $p_z$  orbital at site  $j$ . Here  $U$  and  $V$  denote the strength of on-site and nearest neighbor Coulomb interactions. Estimates of these parameters based on the *ab-initio* methods indicates that even the screened of these parameters in graphene are substantial [14] and on the scale of  $U \sim 10$  eV, which is comparable to corresponding estimates for smaller aromatic molecules [15].

The result of the exact diagonalization for a 16-site honeycomb lattice is shown in Fig. 4. The values of  $U = 9.3$  eV and  $t = 2.8$  eV are adopted from Ref. [14]. For the considered range of  $V$ , the ground state always remains a total singlet state ( $S_0$ ). For small values of  $V$ , the first excited state is the  $T_1$  triplet, followed by a singlet excited state,  $S_1$ . As  $V$  increases, the singlet excited state,  $S_1$  comes down and approaches the energy of  $T_1$  excited state for  $V \approx 3$  eV. Beyond this point, the first excited state will be a singlet state. Thinking from the limit of very large molecules, the  $S_1$  state will

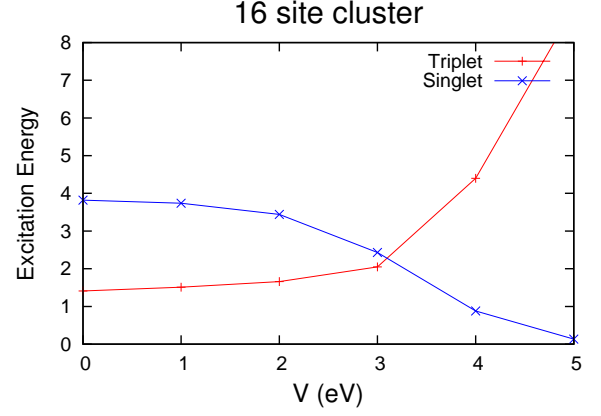


FIG. 4: (Color online) The excitation energy for a 16-site cluster corresponding to  $C_{16}H_{10}$  in the extended Hubbard model. Values of Hubbard  $U$  and  $t$  taken from Ref. [14] are in eV. The ground state always remains a singlet. The first excited states for small values of  $V$  are triplet. By increasing  $V$ , the order of  $T_1$  (red) and  $S_1$  (blue) is switched, and beyond  $V \approx 3$  eV,  $S_1$  will be the first excited state. All energies in this figure are in eV.

have no analogue in terms of plasmon oscillations. Since, first of all, plasmon oscillations require non-neutral system [25] Secondly, long range Coulomb interaction makes the singlet branch either an acoustic plasmon (for 2D coulomb repulsion) or a gapped pi-plasmon (3D coulomb repulsion) branch. So the  $S_1$  state can not be interpreted as molecular analogue of plasmon mode. On the other hand, the decreasing behavior of the  $S_1$  energy with  $V$  is consistent with a doublon-holon interpretation: The repulsion  $V$  among the electrons will become attraction  $-V$  between the doublon-holon pair, and increasing  $V$  will lower their energy.

**Summary and discussions:** We have used *ab-initio* QMC method to obtain an accurate excited state  $T_1$  and an upper bound for the  $T_1$ . We then used exact diagonalization to study a minimal model which captures the same set of excitations. Assuming RVB ground state [6], offers a unified understanding of both states. In this scenario, the  $T_1$  can be understood as the energy required to break a singlet in the RVB background and render it triplet [17]. Moreover, the  $S_1$  can be attributed to a holon-doublon pair created by removing one electron from one carbon site, and placing it in the  $p_z$  orbital of another carbon site. Such charge fluctuations are allowed because the on-site Coulomb energy  $U$  is finite. In this picture, the decrease in  $S_1$  energy by increase in  $V$  becomes quite natural. This interpretation can be a possible description of the collective charge excitations observed in thick multi-wall carbon nano-tubes [26].

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